Hydrothermal fluid pressure-temperature drives CO_2 emission and seismicity at Campi Flegrei (Italy)

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Highlights

- Gas-geoindicators indicate an escalation of the hydrothermal P-T Campi Flegrei
- Pressurization causes increase of the CO_2 emission at Solfatara (up to 5000 t/d)
- Increasing P-T triggers low magnitude earthquakes within the hydrothermal system

Abstract

Fluids supplied by stored magma at depth are causal factors of volcanic unrest, as they can cause pressurization/heating of hydrothermal systems. However, evidences for a link between hydrothermal pressurization, CO_2 emission and volcano seismicity have remained elusive. Here, we use recent (2010-2020) observations at Campi Flegrei caldera (CFc) to show hydrothermal pressure, gas emission and seismicity at CFc share common source areas and well-matching temporal evolutions. We interpret the recent escalation in seismicity and surface gas emissions as caused by pressure-temperature increase at the top of a vertically elongated (0.3-2 km deep) gas front. Using mass (steam) balance considerations, we show hydrothermal pressurization is causing energy

transfer from the fluids to the host rocks, ultimately triggering low magnitude earthquakes within a seismogenetic volume containing the hydrothermal system. This mechanism is probably common to other worldwide calderas in similar hydrothermal activity state.

Keywords
Volcanic unrest, hydrothermal systems, Campi Flegrei, fumarole compositions, CO_2 emission, volcano seismicity

1. Introduction

The injection, ascent, storage and surface release of deep fluids in the upper crust are widespread phenomena in nature, and are recurrent drivers of geological catastrophes. Fluid pressure increase in the upper crust can trigger seismicity reducing the effective normal stress on fault planes (e.g. (Hubbert and Rubey, 1959; Sibson, 1992; Miller, 2013), and the recurrently observed co-seismic variations in gas flux and composition (Fischer et al., 2017; Girault et al., 2018; Chiodini et al., 2020) are clear hints for a cause-effect link between fluids and earthquakes. It is also well-established that artificial fluid injection in the subsurface, and the consequent fluid pressure increase, can lead to seismicity (Ellsworth, 2013; Keranen and Weingarten, 2018).
Volcanoes make no exception, the most notable example being that of Mammoth Mt (California), when the sudden surface burst (in 1990) of huge amounts of volcanic-hydrothermal CO_2 associated to a seismic crisis killed a large portion of the forest (Farrar et al., 1995; Sorey et al., 1998), and repeated increases in diffuse CO_2 emissions accompanied seismic swarms in the subsequent years (Lewicki et al., 2014; Hotovec-Ellis et al., 2018; Pfeiffer et al., 2018; Werner et al., 2014).
Volcanoes are especially suitable natural laboratories for investigating fluid flow - pressure - earthquake associations, because robust and relatively continuous geochemical and geophysical datasets are available. One aspect that is especially relevant to restless volcanoes is that injected fluids are generally hot and H_2O-rich so that, upon ascent, can interact with, and condense into, hydrothermal aquifers: the heating and volumetric expansion of the hosting rocks that result from

condensation of such magmatic steam is a potential additional seismicity driver during volcanic unrest (Chiodini et al., 2015).

The relations among hydrothermal temperature-pressure, fluid flow and earthquakes are here investigated at Campi Flegrei (CFc, Fig. 1a), a restless resurgent caldera formed ~ 39 kyrs ago by the largest caldera-forming eruption in Europe in the last 200 kyrs (Costa et al., 2012). CFc exhibits (since the 1950s) repeated inflation periods (Orsi et al., 1999; Del Gaudio et al., 2010) and seismic crises, which have worried the scientific community as much to suggest an eruption is approaching (Kilburn et al., 2017; Selva et al., 2012). The CFc is undergoing since 2004 a new inflation phase (total maximum vertical displacement of ~ 0.75 m by the time of writing), associated with frequent shallow seismicity, part of which interpreted as originating from fluid transfer processes (Bianco et al., 2004; Saccorotti et al., 2007; Chiodini et al., 2017a; D'Auria et al., 2011; Giudicepietro et al., 2020). At the same time, large compositional variations are being observed in the fumarolic effluents (Caliro et al., 2014; Chiodini et al., 2016), and marked flux increases are being registered in hydrothermal CO_2 release from both fumarolic vents (Tamburello et al., 2019) and soil diffuse degassing structures (Cardellini et al., 2017). The escalating CO_2 emissions, and the concomitant compositional changes in the fumaroles, have been interpreted as signs that magma degassing at depth may have reached a critical condition in which heating and pressurization of the shallower CFc hydrothermal system is occurring at accelerating rate (Caliro et al., 2014; Chiodini et al., 2015; Chiodini et al., 2016). In 2012, the evolution of the monitored geophysical and geochemical parameters induced the Italian Civil Protection (DPC) to raise the CFc alert level from green (calm) to yellow (attention).

Here, we characterise the recent pressure-temperature (P-T from here on) evolution in the CFc hydrothermal system, as inferred from geochemical modelling of fumarolic compositions, and to explore its temporal link with the rates of deeply derived CO_2 emissions and seismicity. To this aim, our multidisciplinary analysis combines results for the chemical compositions of the CFc fumaroles with a set of variables relates to the gas emission, and the earthquakes. We exclude from

our analysis the deformation signals, as their main source area is thought to be deeper than the hydrothermal system this work is focussed on (3-4 km; Amoruso et al., 2014a; 2014b).
Geochemical data (fumarolic compositions and CO_2 fluxes) refer to the hydrothermal sites of Solfatara and Pisciarelli (Fig. 1). Solfatara, a tuff cone formed about 4 ka ago (Smith et al., 2011), is the most active degassing zone of the CFc, being site of numerous fumarolic vents and of a widespread soil diffuse degassing of hydrothermal-volcanic CO_2 (Chiodini et al., 2001; Cardellini et al., 2017; Fig. 1b). The most recent CO_2 flux measurements performed over the entire zone identify a ~ 1 km^2 wide area diffusively emitting deeply derived CO_2 (the so called Solfatara Diffuse Degassing Structure, Solfatara DDS, Fig. 1b). The typical CO_2 flux sustained by the DDS was 1000-2000 t d^{-1} in 2014-2016 period (Cardellini et al., 2017). Significant amounts of CO_2 are also emitted by fumarolic vents, the most active of which are located in the eastern slope of the Solfatara cone (Pisciarelli vents, CO_2 emission up to 600 t d^{-1} in 2019 (Tamburello et al., 2019) and inside the Solfatara depression (BG and BN vents, CO_2 emission up to ~ 300 t d^{-1} in 2013; Aiuppa et al., 2013; Pedone et al., 2014; Fig. 1b).
After a description of the evolution over time of different parameters we attempt at an integrated analysis aimed at understanding the impact of hydrothermal fluid P-T changes on earthquakes occurrence and fluid emissions.

2. Material and methods

2.1. Used databases

The databases used in this work (Supplementary Data File S1) are here briefly described.

2.1.1. Chemical compositions of Solfatara fumaroles.

The main and hottest fumaroles of Solfatara, BG (T=150-165°C) and BN (T 140-150°C) (Fig. 1b), have been systematically sampled since 1983 and 1995, respectively. The dataset includes the temperature and chemical compositions (H_2O, CO_2, Ar, N_2, H_2, CH_4 and CO) of gas samples taken and analysed with similar procedures, from 1983 to 2020 (see Caliro et al. (2007) and Cioni and Corazza (1981) for the sampling and analytical methods). This Solfatara fumarolic fluid database is unique for the large number of samples (671), for its continuity (~ 35 years of observations) and for the homogeneity of the sampling and analytical methods used. Different laboratories contributed to this database: the laboratories of CNR of Pisa that started the work at the beginning of 1980's; the laboratory of University of Perugia that analysed the gas samples in the middle 1990's; and the fluid geochemistry laboratory of Osservatorio Vesuviano from 1998 to 2020.

2.1.2. Diffuse CO_2 flux from the Solfatara crater target area.

During April 2004 - October 2020, 149 soil CO_2 flux campaigns have been performed inside the Solfatara crater. In total, the dataset consists of 9315 measurements performed with the accumulation chamber method (Chiodini et al., 1998) over a grid of 63 points whose location remained unchanged during the period (Fig. 1b). The data are reported in monthly surveillance reports of Osservatorio Vesuviano for the Civil Defence of Italy (http://www.ov.ingv.it/ov/it/bollettini/275.html). The results of the first 50 campaigns have already been published (Granieri et al., 2009), while the remaining are here reported for the first time. For each campaign, we computed the total CO_2 output (FCO2 in t d^{-1}) from the target area (Fig. 1b). The FCO2 and its uncertainty were computed by applying a geostatistical method based on sequential Gaussian simulation (sGs; Cardellini et al., 2003) to the soil CO_2 fluxes of the 149 campaigns. Specifically, we used the *sgsim* algorithm (GSLIB software library; Deutsch and Journel, 1998). The CO_2 flux has been simulated on a of 4 × 4 grid m starting from variogram models fitting the experimental variograms of the normal scores of the CO_2 flux (for further details see Cardellini et al., 2003). For each campaign, 200 simulations were realised and the total CO_2 release was computed by summing the products of the simulated CO_2 flux value at each grid cell by the cell surface. The mean total CO_2 flux and its standard deviation, computed from the 200 realizations, are taken as FCO2 and its uncertainty for each campaign. As an example, Supplementary Fig. S1 illustrates the CO_2 flux map obtained considering at each location the mean of the CO_2 fluxes measured in the 149 campaigns. The target area to which each FCO2 estimate refers to (coloured area in Supplementary Fig. S1) was limited to the area within the outermost measuring points, in order to avoid uncertainties related to extrapolations to un-sampled zones.

2.1.3. Diffuse CO_2 flux from the Solfatara DDS.

This dataset includes the total CO_2 output by diffuse degassing at Solfatara (FCO2-DDS) from 1998 to 2016 estimated form soil CO_2 flux measurements covering an area of 1.4 km^2 which includes Solfatara crater and Pisciarelli areas (Fig. 1b; Cardellini et al., 2017). The soil CO_2 fluxes were measured in 30 surveys using the accumulation chamber method (Chiodini et al., 1998) and the total CO_2 output was estimated applying a geostatistical method based on sGs (for further details see Cardellini et al., 2017).

2.1.4. CO_2 fluxes from Pisciarelli vents.

This dataset is composed of twenty-one measurements of the CO_2 flux from the Pisciarelli vents performed by different authors during 2012-2019 (Aiuppa et al., 2015; Aiuppa et al., 2013; Pedone et al., 2014; Queißer et al., 2017; Tamburello et al., 2019). Measurement methods are different and include: tunable diode laser absorption spectroscopy (Pedone et al., 2014), differential absorption lidar (Aiuppa et al., 2015), laser remote-sensing spectrometry (LARSS; Queißer et al., 2017), multi-component gas analyzer system (MultiGAS; Aiuppa et al., 2013; Tamburello et al., 2019). The reader is referred to the original articles for the details on these different techniques.

2.1.5. Fumarolic tremor at Pisciarelli.

The fumarolic tremor is a continuous seismic signal recorded in the vicinity of the Pisciarelli fumaroles, currently the largest of the CFc. To record this signal, a seismic station was installed in 2010 about 8 m away from the main fumarolic vent. The fumarolic tremor, analyzed in previous studies (Chiodini et al., 2017b; Giudicepietro et al., 2019; Giudicepietro et al., 2020), is polarized in the vertical direction and characterized by a spectral peak at around 10 hz. To represent the temporal evolution of the tremor amplitude, the Real-time Seismic-Amplitude Measurement (RSAM; Endo and Murray, 1991) was calculated on 30-minute windows of the vertical component signal, filtered in 5 -15 Hz frequency band.

2.1.6. Air CO_2 concentrations at Pisciarelli.

Since April 2007, an automatic station measures soil temperature, soil CO_2 fluxes, and CO_2 concentrations in air, at 40 cm height, 20 m downwind of the main Pisciarelli vent (Chiodini et al., 2017b). The April 2007-October 2020 daily air CO_2 concentrations are systematically higher than in ambient air (1000-5000 ppm vs ~ 400 ppm) due to persistent fumigation from the fumarolic plume.

2.1.7. Earthquakes

We used the CFc earthquake locations available in the public-access INGV- Osservatorio Vesuviano database (http://sismolab.ov.ingv.it/sismo/index.php?PAGE=SISMO/last&area=Flegrei). Hypocentral locations were obtained using a 1D layered velocity model. The dataset consists of 2026 located earthquakes with magnitude (Md) ranging between -1.1 and 3.3, representing about 47% of the total number of CFc earthquakes recorded by the INGV-Osservatorio Vesuviano permanent seismic network between January 2004 and October 2020. Seismicity is mostly concentrated in the Solfatara-Pisciarelli area (Fig. 1a) at relatively shallow depth and the magnitude of the events is generally low with only 16 events with $2.0 \leq Md \leq 3.3$. From 2005 to 2012, earthquakes occurred mainly in swarms. Since 2012-2013, their occurrence rate has increased over time, both as swarms and as single events, with single events becoming more frequent in the last 2 years.

3. Results and Discussion

3.1. Pressure-temperature geoindicators based on fumarole compositions

Since 1984, the Solfatara compositional database was used to derive the T-P conditions of the feeding system (e.g., Cioni et al., 1984; Chiodini et al., 1996; Caliro et al., 2007; Chiodini et al., 2015; Chiodini et al., 2016). Recently, two different geochemical approaches have lead to contrasting results and different implications for the current CFc unrest, which has been interpreted as either driven by pressurization of the CFc system (Chiodini et al., 2015; Chiodini et al., 2017a), or associated with a general depressurization of the hydrothermal system (Moretti et al., 2017) (Fig. 2). We refer to the two approaches, which stand on different model assumptions, as the *no-condensation* (Moretti et al., 2017) and *vapour-liquid coexistence* (Chiodini et al., 2015) models.

3.1.1. The no-condensation model

Moretti et al. (2017) applied a model originally developed by Chiodini et al., (1996) and then refined by Chiodini and Marini (1998). The geobarometric and geotermometric relations are derived considering the formation reactions of H_2, CO and CH_4 from the main species H_2O and CO_2:

$$H_2O \leftrightarrow H_2 + 1/2\ O_2 \qquad (1)$$

$$CO_2 \leftrightarrow CO + 1/2\ O_2 \qquad (2)$$

$$CO_2 + 2\ H_2O \leftrightarrow CH_4 + 2\ O_2 \qquad (3)$$

whose equilibrium constants are expressible as:

$$\log K_{H2} = \log f_{H2} + 1/2 \log f_{O2} - \log f_{H2O} \qquad (4)$$

$$\log K_{CO} = \log f_{CO} + 1/2 \log f_{O2} - \log f_{CO2} \qquad (5)$$

$$\log K_{CH4} = \log f_{CH4} + 2 \log f_{O2} - \log f_{CO2} -2 \log f_{H2O} \quad (6)$$

where $\log K_{H2} = -12707/T + 2.548$, $\log K_{CO} = -14955/T + 5.033$ and $\log K_{CH4} = - 42007/T + 0.527$ (thermodynamic data from Stull et al. (1969)). Suitable combinations of equations 4, 5 and 6 allow to eliminate the log f_{O2} variable and to derive the following geothermometric and geobarometric functions:

$$T = -2248 / (\mathrm{Log}\ X_{CO}/X_{CO2} + \mathrm{Log}\ X_{H2O}/X_{H2} - 2.485) \quad (7)$$

$$\mathrm{Log}\ P_{H2O} = (19.605 - \mathrm{Log}\ (X_{CO}^{4}/(X_{CH4} \times X_{CO2}^{3}) -17813/T)/2 \quad (8)$$

where the equimolar ratios of the measured fumarolic molar fractions (X_i) are assumed equal to the fugacities ratios and $P_{H2O} \sim f_{H2O}$. .

Finally considering the Dalton law,

$$P_{CO2} = P_{H2O}\, X_{CO2} / X_{H2O} \quad (9)$$

$$Ptot \sim P_{CO2} + P_{H2O}. \quad (10)$$

Relevant assumptions of this approach are: (i) the redox conditions are internally fixed within the H_2O-CO_2-H_2-CO- CH_4 gas system, an assumption that implies that CH_4 equilibrates at the same T-P conditions as the kinetically faster species H_2 and CO (Giggenbach, 1987); (ii) no secondary processes affect H_2O (condensation and/or water addition). Because the contrasting results with the model of Chiodini et al. (2015) strongly depends on this last assumption, we name the model used by Moretti et al. (2017) as the *no-condensation* model.

3.1.2. The vapor-liquid coexistence model

Caliro et al. (2007) considering the carbon isotopic exchange reaction between CO_2 and CH_4, demonstrated that the CH_4/CO_2 ratio reflects temperatures (360-430°C) much higher than those returned by the H_2/H_2O and CO/CO_2 ratios (200-250°C). Furthermore, starting from early 2000's, macroscopic evidences suggested the occurrence of secondary processes (i.e. steam condensation) affecting the fumarolic H_2O content: (i) the almost continuous increase in the incondensable gas fraction relative to water (Chiodini et al., 2015); (ii) a systematic increase of the CO/CO_2 ratio (an indicator of hydrothermal temperature, and condensation is very efficient to heat a hydrothermal system); (iii) the pervasive circulation of condensates underneath Solfatara crater, and in particular close to the main fumaroles BG and BN (Bruno et al., 2007; Byrdina et al., 2014; Gresse et al., 2017); (iv) the formation of a strong boiling pools of condensates and repeated episodes of liquid/mud emission at Pisciarelli (Chiodini et al., 2015).

In order to avoid the effects of these secondary processes affecting H_2O, and in order to exclude CH_4 from the model, Chiodini et al. (2015) derived T-P functions from equations 4 and 5 based on equimolar ratios between incondensable gases (H_2, CO, CO_2). The derivation of the geothermometric and geobarometric function was possible considering (i) f_{H2O} fixed by the vapour-liquid coexistence and (ii) f_{O2} as a function of the temperature. Redox conditions of Solfatara gases were assumed to be controlled by a typical redox buffer for hydrothermal system (DP buffer; D'Amore and Panichi, 1980) , $\log f_{O2} = 8.20 - 23643/T$). According to Chiodini and Marini (1998), an alternative f_{O2}-T function applicable to Solfatara fumarolic gases is the 'Campanian Volcanoes' buffer (CV, $\log f_{O2} = 7.75 - 23169/T$). The correspondent geothermometric relations are:

$$T = 3133.5 / (0.933 - \text{Log } X_{CO}/X_{CO2}) \quad (11)$$

valid for redox conditions controlled by the DP relation, and

$$T = 3370.5 / (1.158 - \text{Log } X_{CO}/X_{CO2}) \quad (12)$$

when considering the CV redox buffer.

The geobarometric functions are:

$$\text{Log } P_{H2O} = 5.510 - 2048/T \quad (13)$$

where the water pressure is assumed equal to water fugacity of saturated vapor (i.e. vapor-liquid coexistence for pure water (Giggenbach, 1980)),

$$\text{Log } P_{CO2} = 3.025 + 201/T - \text{Log } X_{H2}/X_{CO} \quad (14)$$

derived by a linear combination of equations 4 and 5, and

$$Ptot \sim P_{CO2} + P_{H2O.} \quad (15)$$

Use of either the DP or the CV f_{O2}-T relation results into different P-T estimations. In agreement with Chiodini et al. (2015), we use the DP option (equation 11) that, for the post 2010 period considered in this work (see Fig. 6), outputs T values from 218°C to 267°C and P from 27 to 60 bar; while the alternative equation 12 (CV buffer) returns higher T and P values (238°C - 287°C, 37 bar - 78 bar). We stress, however, that these systematic differences do not affect the results and considerations of our work that is based on the relative variation of the normalised T-P values that are practically the same for both the DP and CV estimations.

We will refer to this model as the *vapour-liquid coexistence* model.

3.1.3. Temperature-Pressure estimations

The T-P estimates, derived by the two models for the entire Solfatara fumaroles' database, are contrasted in the chronograms of Fig. 2.

Even tough, any model can not be considered completely reliable because it is necessarily based on some a-priori assumptions, the *no-condensation model* is certainly not reliable because the total estimated pressures (Ptot = P_{H2O} + P_{CO2}) for the post-2015 samples are impossible as systematically below atmospheric pressure (<1 bar, Fig. 2b).

The reliability of the *vapour-liquid coexistence* model is tested below by comparing the inferred P-T conditions with different independent fluid flow related variables, and with the earthquake occurrence at CFc.

3.2. Fluid flow related (FFR) variables

Figures 3a, b ,c, d and e are chronograms of the available FFR variables that we take as proxies for the CO_2 degassing regime of the Solfatara-Pisciarelli area. In particular the CO_2 flux (FCO2, Fig. 3a) from the Solfatara target area (see Fig. 1b) and the total CO_2 flux from the entire Solfatara DDS (FCO2-DDS, Fig. 3b; Cardellini et al., 2017) are representative of the diffuse emission. Numerous

FCO2 data (149) are available for the entire observation period (2004-2020) while FCO2-DDS measurements are less frequent (Cardellini et al., 2017) and not available since 2017.
The CO_2 flux from Pisciarelli vents (Fig. 3c; Tamburello et al., 2019), the fumarolic tremor at Pisciarelli (RSAM, Fig. 3d) and the CO_2 concentrations in air at Pisciarelli (air CO_2, Fig. 3e) are taken as proxies of the vent emission in the area. Although not direct flux measurements, RSAM and air CO_2 are almost continuously acquired, and their temporal fluctuations have previously been shown to scale with the intensity of hydrothermal activity at Pisciarelli (Fig. 4; Chiodini et al., 2017b; Giudicepietro et al., 2019; Giudicepietro et al., 2020).

3.3. 2004-2020 earthquakes occurrence at CFc

We refer here to the earthquakes occurred at CFc from 2004 to October 2020 (Fig. 1a) whose locations and magnitudes are available in public databases of the Osservatorio Vesuviano (http://www.ov.ingv.it/ov/it/banche-dati.html; see Material and Methods). It is worth to note that the events concentrate underneath the Solfatara-Pisciarelli (Fig. 1a) and are in general of low magnitude (maximum magnitude = 3.3) and of relatively shallow depths (Fig. 5a). The earthquakes' occurrence rate manifestly increases since 2017-2018 (Fig. 5b). Note that Fig. 5b reports events with magnitude ≥ 0.1, for which the catalogue is reasonably complete in the observation period. The absence of deep events at CFc (i.e. depth >3-4 km) likely reflects the high temperatures expected at depth, and a very shallow brittle-ductile transition (3-5 km; Castaldo et al., 2019).

3.4. Comparison of the different datasets

A multivariate time-series analysis is attempted to compare the different observations. To this aim, we compute the annual mean (annual number for the earthquakes) of each variable (red points in Figs. 2, 3 and 5), focussing on the 2010-2020 period, for which most of the variables are available. The approach based on the analysis of the annual values has the advantage of filtering out any seasonally controlled variations. The multivariate analysis is not applied to the FCO2-DDS (Fig.

3b) and to the CO_2 flux from Pisciarelli vents *(*Fig. 3c) because these measurements are sporadic and not available for the entire period. In detail, a Principal Component Analysis (PCA) was performed on the other FFR variables (air CO_2, FCO2, RSAM) and earthquakes to simplify and summarize the relationships among the multivariate set of data. We used the function *prcomp* of the package *stats* of the R software (R Core Team, 2018), which performs PCA via a singular value decomposition of the centered and scaled data matrix. This technique derives a new set of uncorrelated variables (Principal Components, PC) using a linear combination of the original variables, and ranks them in terms of their overall control on the variance. PCA is therefore used to reduce the dimensionality of the data set, by choosing only those PCs that explain most of the variance in the data. In practice, the PCA applied to the 4-variables matrix returns 4 PC, which retain different proportions of the total variance: PC1 the 93.6%, PC2 the 3.9%, PC3 the 1.8%, and PC4 the 0.7% (Table 1). The scores of these new variables are calculated multiplying the matrix of the scaled original variables by the eigenvector matrix in Table 1 (namely, the eigenvectors of the correlation matrix of the original data set). These results indicate that nearly the total (temporal) variability of the data (~94%) is explained by PC1 only, which is defined by an almost identical contribution of air CO_2, RSAM, FCO2, and Earthquakes variables (see the coefficients of the first eigenvector in Table 1).

This suggests that a single driving mechanism controls the variations of hydrothermal fluid flux and earthquakes (Fig. 6), and as such summarizes well the temporal evolution of the hydrothermal part of the CFc unrest. It is worth to note that PC1 is very well correlated with the Ptot and temperature, estimated using the *vapour-liquid coexistence* model (Fig. 6). This supports our hypothesis that increasing fluid pressure and temperature in the hydrothermal system is a causal factor in triggering the CFc seismicity, and is the driver for the observed escalation in hydrothermal fluid release at the surface.

In contrast, the *no-condensation* model outputs unrealistic results, as post-2015 estimated pressures are unacceptably low (< atmospheric pressure, 1 bar) and decrease over the same temporal interval during which earthquake occurrence rate and surface hydrothermal fluid fluxes are both visibly increasing. This mismatch indicates that the assumption that fumarolic water concentrations are currently fully representative of the deep, equilibrium compositions (Moretti et al., 2017) is inconsistent with the observations.

3.5. The conceptual model of the hydrothermal system and 'hydrothermal' seismicity

The conceptual model based on the *vapour-liquid coexistence* assumption is sketched in Fig. 7a over a 2-D resistivity model of Solfatara, derived by AMT (AudioMagnetoTelluric) measurements (Siniscalchi et al., 2019). The section is dominated by a ~2 km long vertically elongated resistivity structure in axis with Solfatara. This is the core of the hydrothermal system feeding the Solfatara-Pisciarelli hydrothermal sites. It is interpreted as a permeable zone that favours gas ascent from the hottest and deepest portions of the system. Hot, methane-free magmatic fluids enter the base (> 2 km depth) of the system, mix with and vaporize meteoric liquids, and ultimately create the condition for CH_4 formation at temperatures > 360°C (Caliro et al., 2007). From that zone, a gas plume rises up to 0.3-0.7 km where the resistive structure is interrupted by conductive layers (green, cyan and blue colours) that reflect both hydrothermal altered zones and a liquid phase-dominated environment (Siniscalchi et al., 2019). It is worth to note that, assuming a hydrostatic control on fluid pressure, the inferred equilibration pressures of the *vapour-liquid coexistence* model (from 30 to 80 bar, considering both the DP and CV redox buffers, see section 3.1.2) correspond to gas equilibration depths of 0.3-0.8 km, that coincide with the top of the resistive structure (Fig. 7). Here, at the interface with the overlying clayed altered zones, the gas phase is expected to accumulate and to reside for a sufficient time to allow the gas phase to re-equilibrate at the local T-P conditions. From that zone, the gas moves toward the surface trough fractures, shallow gas pockets and liquid bodies whose existence and complex geometry has been highlighted by detailed geo-electric surveys (Byrdina et al., 2014; Gresse et al., 2017; Gresse et al., 2018).

According to (Chiodini et al., 2016), an escalating magmatic fluid inflow at the base of the hydrothermal system causes its heating and pressurization, and in turn the increase of the CO_2 emission at the surface and seismicity (Fig. 6). A dense earthquake cluster is observed at 0.5-1 km depth (Fig. 7b and c), and since this interval nicely corresponds to the gas equilibration depths inferred above (0.3-0.8 m) is here interpreted as the head of the gas front feeding the hydrothermal system. Thus, our inferred Ptot increase refers to such topmost portion of this seismogenetic vertical gas plume. It is also noteworthy the existence of a second, deeper (>2 km) seismicity cluster that corresponds to the source area irradiating the highest magnitude earthquakes (Fig. 7b): this structure has been interpreted as the root of the gas plume, in which larger events are likely caused by pulsed magmatic fluid injections (e.g., Giudicepietro et al., 2020).

Ultimately, the close spatial correspondence between the main seismogenetic volume (0.5-1 km) and the gas equilibration zone (0.3-0.8 km) supports the idea that, similarly to the seismicity induced by anthropogenic fluid injection, the generalised pressurization and heating of the CFc gas dominated-hydrothermal system act as the main seismicity trigger (Fig. 7b and c).

3.6. A mass balance of the steam associated with the CO_2 emission and hydrothermal seismicity

The observed escalation in surface gas release at Solfatara and Pisciarelli is an additional evident sign for increased gas transport at depth, and of a generalised gas pressure build-up at source. Using the numerous data of the CO_2 emission from the target area (FCO2, Fig. 3a) we compute that the total CO_2 emissions from Solfatara DDS increased from ~ 1000 t d^{-1} in 2008-2010 up to 3000-4000 t d^{-1} in 2019-2020 (Fig. 8). Considering that similar increments also affected the fumarolic vents (Tamburello et al., 2019) we can roughly estimate the current total CO_2 emission from Solfatara-Pisciarelli at ~ 5000 t d^{-1}. This flux ranks CFc among the first 8 top volcanic CO_2 emitters on Earth (Fischer et al., 2019; Werner et al., 2019). Such an unusually large gas supply implies pressure-build up in the gas source area (the hydrothermal system), and must inherently be associated with a large thermal energy release (as steam and CO_2 are associated prior to condensation). We stress that since gas pressurization is an exothermic process, it may itself be causing heating. In addition, the pressurization of a steam-rich gas phase can induce its condensation, a process that at CFc hydrothermal system is described by the *vapour-liquid coexistence* geochemical model. Condensation can be shallow (forming the hot soils and mud pools that characterise the fumarolic fields) or relatively deep. We attempt at establishing a steam mass balance for the hydrothermal systems by dividing it into 3 components (Fig. 9a):

- the original steam emission at reservoir conditions (*reservoir emission* in Fig. 9a); this is derived by multiplying the diffuse CO_2 flux (FCO2-DDS) by the H_2O/CO_2 ratio in the gas equilibration zone (derived from P_{H2O} and P_{CO2} estimates);
- the fraction of steam condensing in the sub-surface of the DDS (*DDS condensate* in Fig. 9a); this computed by multiplying FCO2-DDS by the fumarolic H_2O/CO_2;
- the fraction of steam that condense at depth (*deep condensate* in Fig. 9a, b and c); given by the difference *reservoir emission* - *DDS condensate*.

It is worth to note that the inferred temporal evolution of the *deep condensate* mass match nicely that of ‘hydrothermal’ seismicity (Fig. 9b and c), i.e. of the events occurred in the volume containing the hydrothermal system (see Fig. 7b and c). In our interpretation, the *deep condensate* represents the fraction of the original steam/thermal energy budget that can potentially trigger earthquakes because the condensed liquid can lubricate pre-existing fractures and because hydrothermal host rocks get hotter, increase in volume by thermal dilatation, and finally fracture as they reach a failure threshold. The total thermal energy involved in *deep condensation* from 2004 to 2020 is $\sim 4\times10^{14}$ J (computed from the latent heat of condensation), and is thus well enough to justify the observed seismicity (being 5 orders of magnitude higher than the cumulative energy of all the CFc earthquakes, $\sim 1.5\times10^{9}$ J, http://www.ov.ingv.it/ov/bollettini-mensili-campania/Bollettino_Mensile_Campi_Flegrei_2020_10.pdf).

4. Conclusions

We use a novel multidisciplinary approach to characterise the spatial-temporal evolution of the hydrothermal unrest currently affecting CFc. A multivariate analysis shows that different datasets, including a set of fluid flow-related variables and earthquake occurrence, share a common evolution during 2010-2020, and are fully described by a single component that explains 94% of their total variance. This component, whose values exhibit a sharp increase from 2018 onward, is well correlated with escalating pressure and temperature of the hydrothermal system inferred from geochemical modelling of fumarole composition. The P-T increase occurs in a gas-dominated zone, located at depths of < 1 km below the main hydrothermal sites, which corresponds to the main cluster of low magnitude, post 2004 earthquakes. This temporal and spatial association between hydrothermal P-T and seismicity brings compelling evidence for the role played by pressurising hydrothermal fluids in driving volcano seismicity at CFc. Our results bring evidence for the seismogenetic role played by magmatic gas injection into hydrothermal systems, and are thus of general relevance for other volcanoes in similar contexts.

Acknowledgments:

We would like to remember the researchers Roberto Cioni and Egizio Corazza who recently passed away: they began to sample and analyze Solfatara fumaroles in early 1980's, starting the Solfatara fumaroles database.

Funding: This work was supported by MIUR, project n. PRIN2017-2017LMNLAW "Connect4Carbon".

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Table 1. Principal Component Analysis (PCA). Results of the PCA applied to the variables FCO2, RSAM, air CO_2 and earthquakes.

	Eigenvectors			
Variables	**PC1**	**PC2**	**PC3**	**PC4**
FCO_2	0.4993	0.3342	-0.7991	0.0215
RSAM	0.5100	-0.0659	0.2692	-0.8143
air CO_2	0.4914	-0.7896	-0.0134	0.3672
earthquakes	0.4992	0.5103	0.5373	0.4491
Importance of components	**PC1**	**PC2**	**PC3**	**PC4**
Variance	3.7591	0.1430	0.0736	0.0243
Proportion of variance	0.9398	0.0357	0.0184	0.0061
Cumulative proportion	0.9398	0.9755	0.9939	1.0000

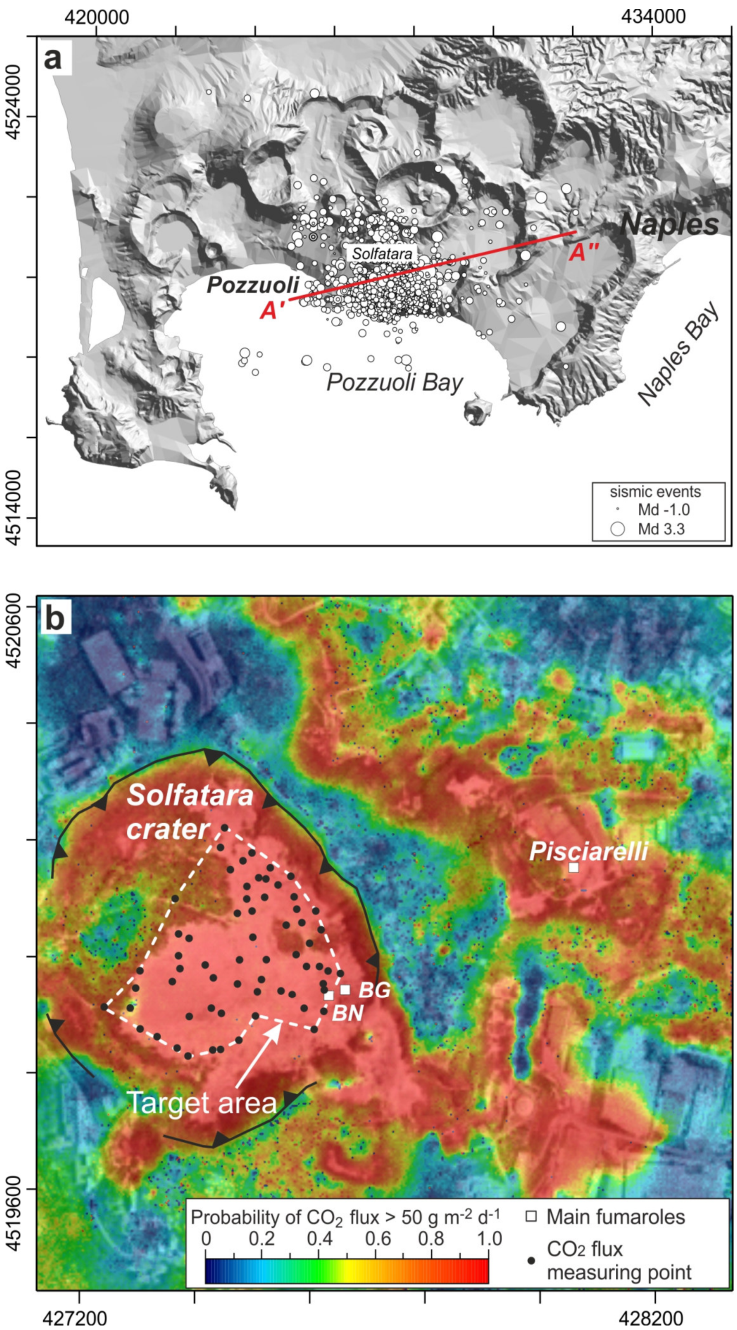


Fig. 1. Location map. a) Campi Flegrei caldera and location of the 2004-2020 earthquakes. The A'-A'' line refers to the vertical section reported in Fig. 6. b) Map of the Solfatara diffuse degassing structure (DDS) showing the locations of the target area, the monitored 63 points and the main fumaroles. The map, based on 13,158 CO_2 flux measurements from 1998 to 2016 (Cardellini et al., 2017), illustrates the probability that the simulated CO_2 flux is greater than 50 g m^{-2} d^{-1}, selected as the threshold for a pure biogenic CO_2 flux. Coordinates are expressed in UTM-WGS84

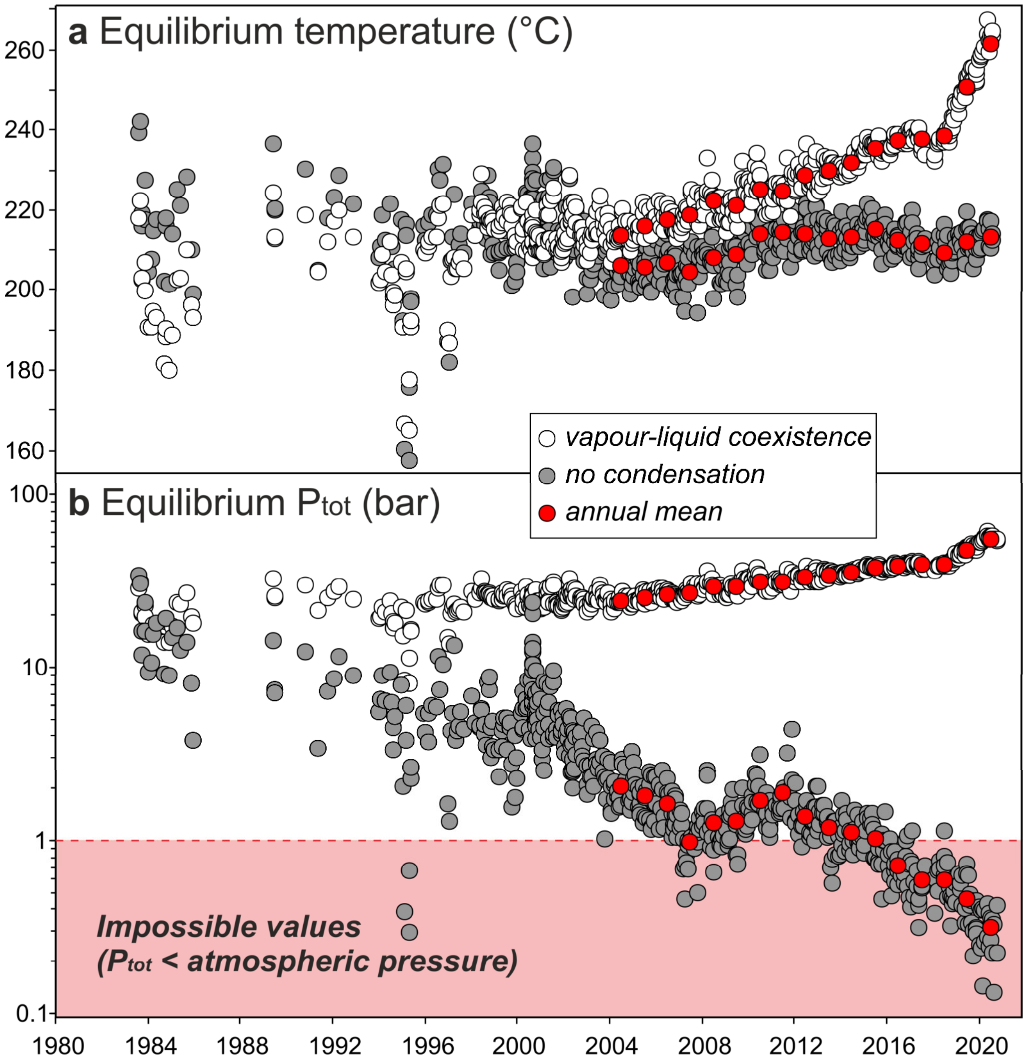


Fig. 2. T-P estimates. a) Equilibrium temperatures and b) pressures estimated with two alternative geochemical models (see the text) from the 1983-2020 compositions of BG and BN fumaroles.

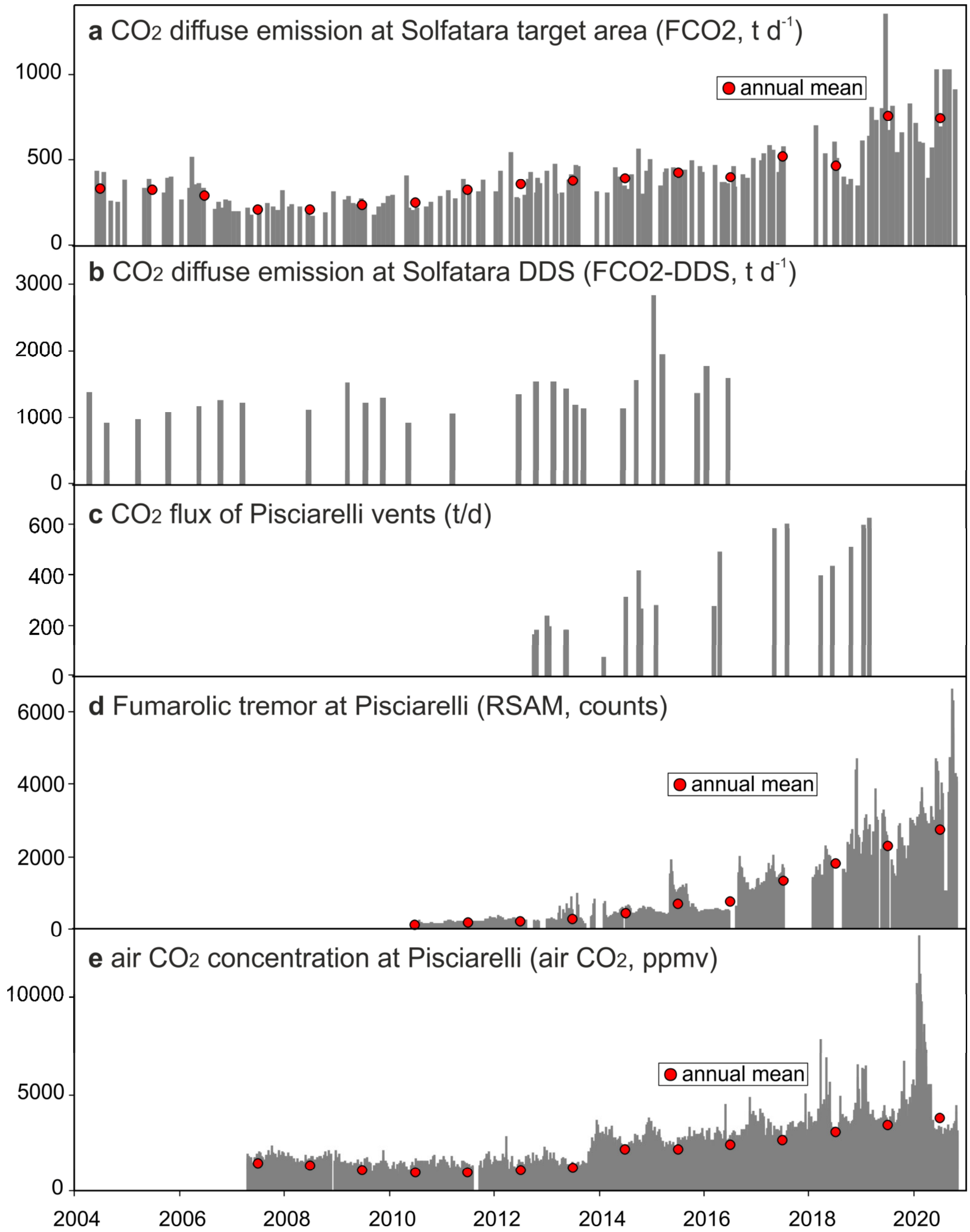


Fig. 3. Chronograms of the FFR variables. Annual means are reported with red symbols.

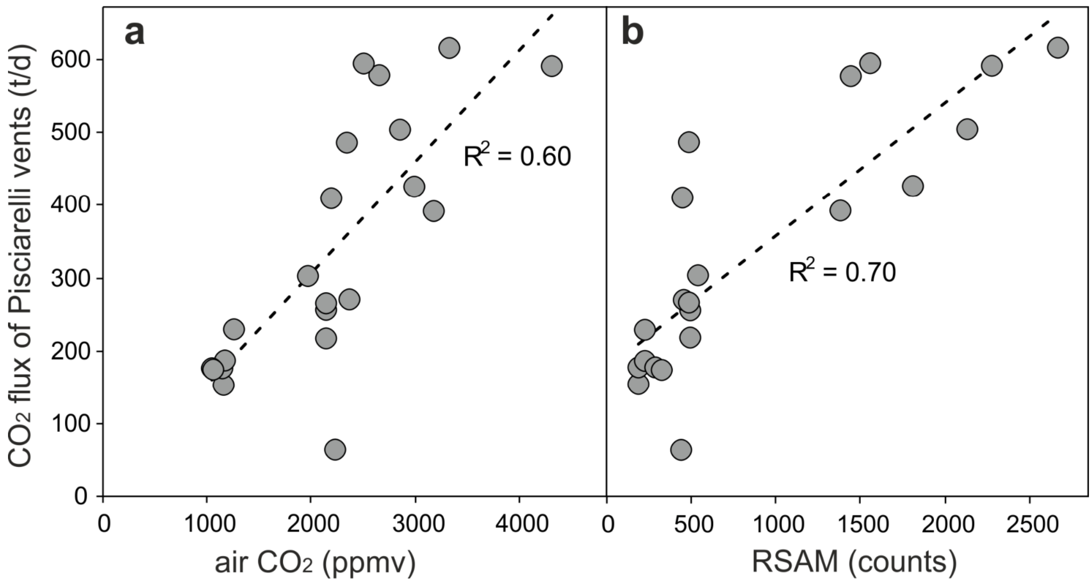


Fig. 4. air CO_2 and RSAM vs CO_2 flux of Pisciarelli vents. RSAM and air CO_2 are reported as the mean values measured at the time of the CO_2 flux campaign ± 30 days.

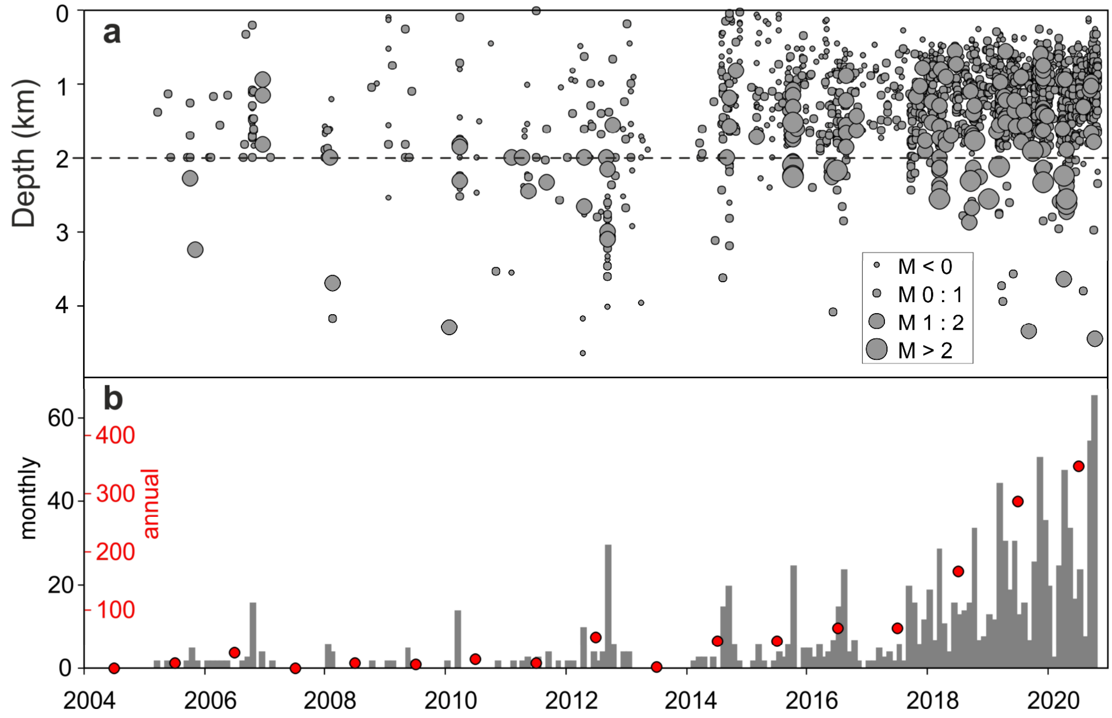


Fig. 5. CFc earthquakes from 2004 to October 2020. a) chronogram of depths and magnitudes; b) monthly (gray histogram) and annual (red symbols) number of earthquakes with Magnitude > 0.1 ; the 2020 annual number of earthquakes has been scaled over the entire year.

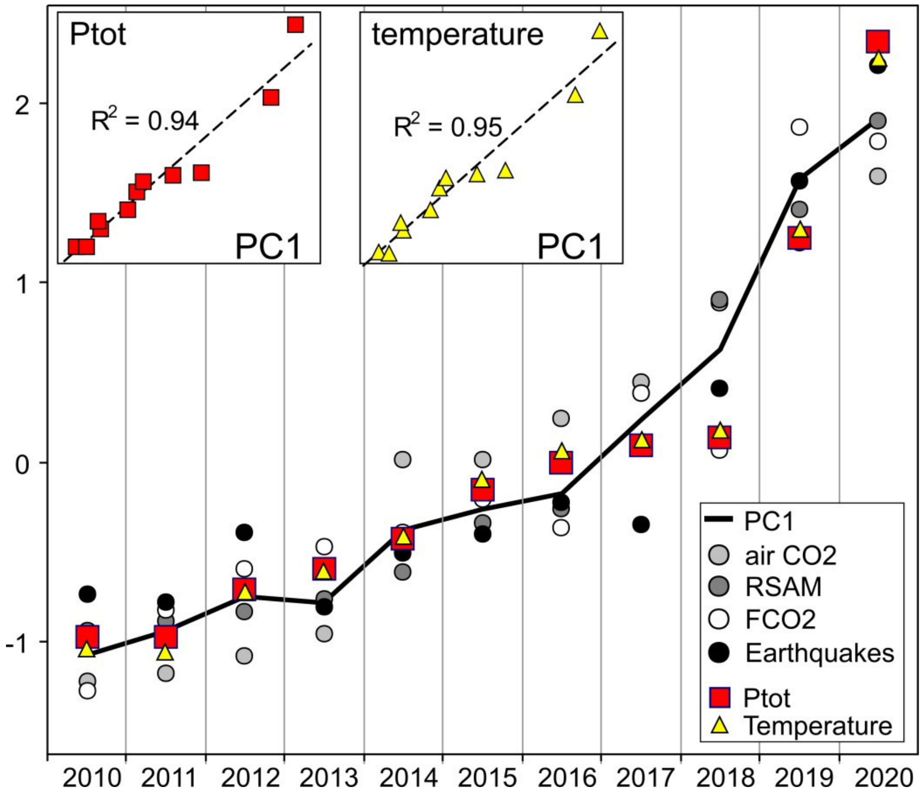


Fig. 6. Results of the PCA and Ptot. Chronograms of the z-scores of the FFR variables (air CO_2, RSAM, FCO2), earthquakes occurrence, PC1, and the Ptot-temperature estimations based on the *vapour-liquid coexistence model* (all the variables are reported as annual means; the z-score is equal to the variable minus the mean divided for the standard deviation). The FFR variables and the Earthquakes occurrence were analysed with a PCA and PC1 is the resulting main component explaining their 94% total variance. PC1 is plotted against Ptot and temperature in the insets.

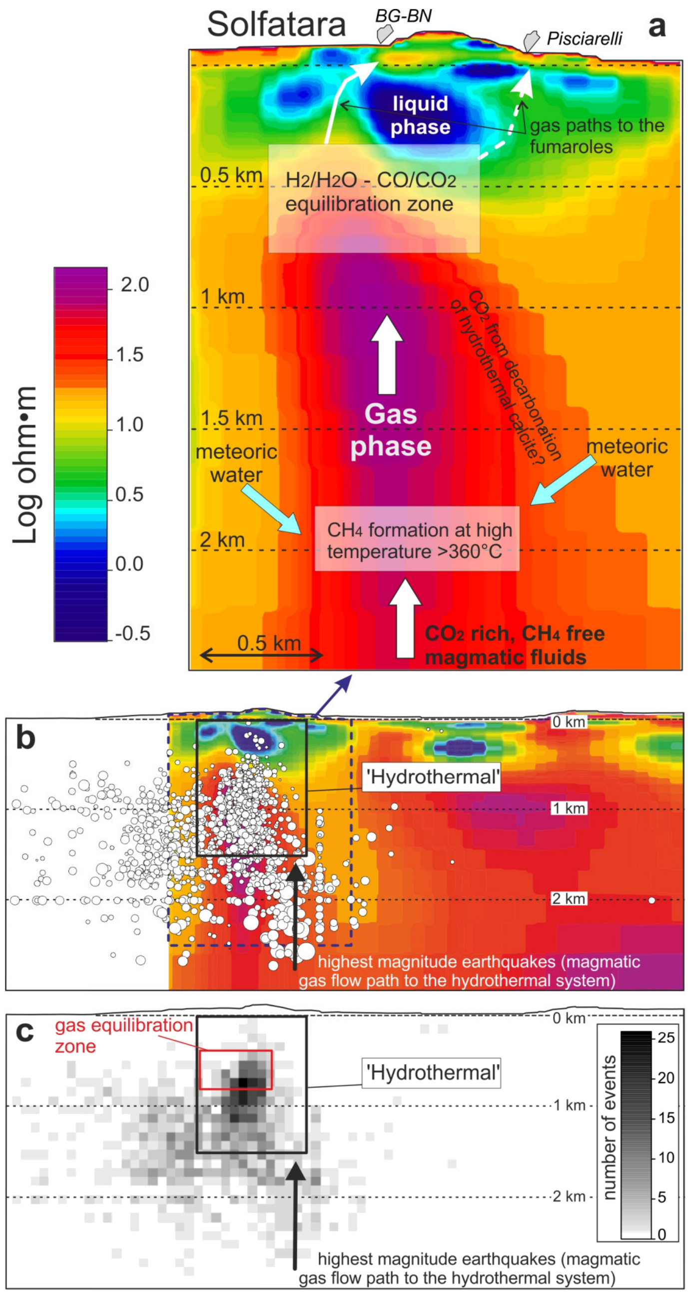


Fig. 7. Conceptual model and seismicity. a) Geochemical conceptual model of the hydrothermal system feeding the Solfatara-Pisciarelli manifestations sketched over a resistivity section (redraw from Siniscalchi et al. (2019)). b) section (A'-A'' in Fig. 1A) showing the relations between earthquake location (distance < 0.6 km from the section) and resistivity. The dimension of the white circles is proportional to the magnitude of the events. c) 2 D density map of earthquakes in the A'-A'' section (computed as the number of events projected on cells of 100×100 m^2). The 'hydrothermal' box is a section of a parallelepiped of 1.2×1.2×1.5 km assumed to contain the hydrothermal system (see the text and Fig. 9).

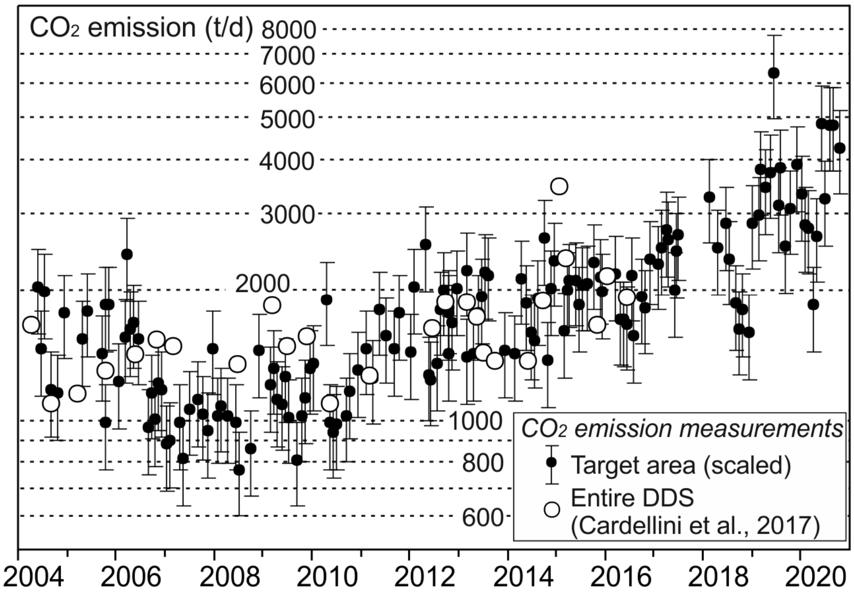


Fig. 8. CO_2 emission from diffuse degassing at Solfatara DDS during 2004-2020 The black dots refer to the emission from the target area (Fig. 1 and Fig. 3a) scaled over the entire DDS. This was possible by elaborating the data of the 30 campaigns reported in (Cardellini et al., 2017). From these data we computed the mean ratio between the DDS emission and that from the target area (4.7±1.1), that is used as correction factor (error bars refer to the standard deviation of the correction factor)

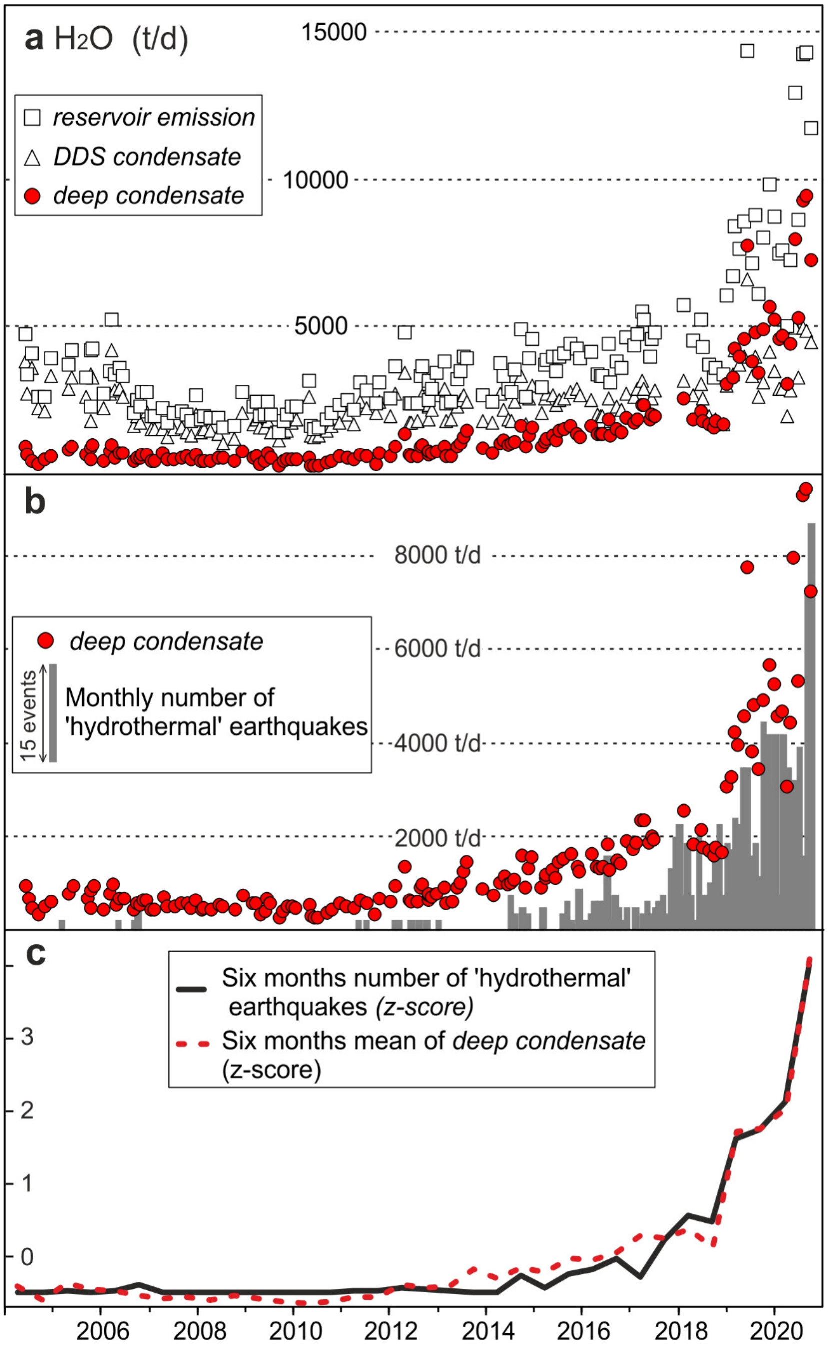
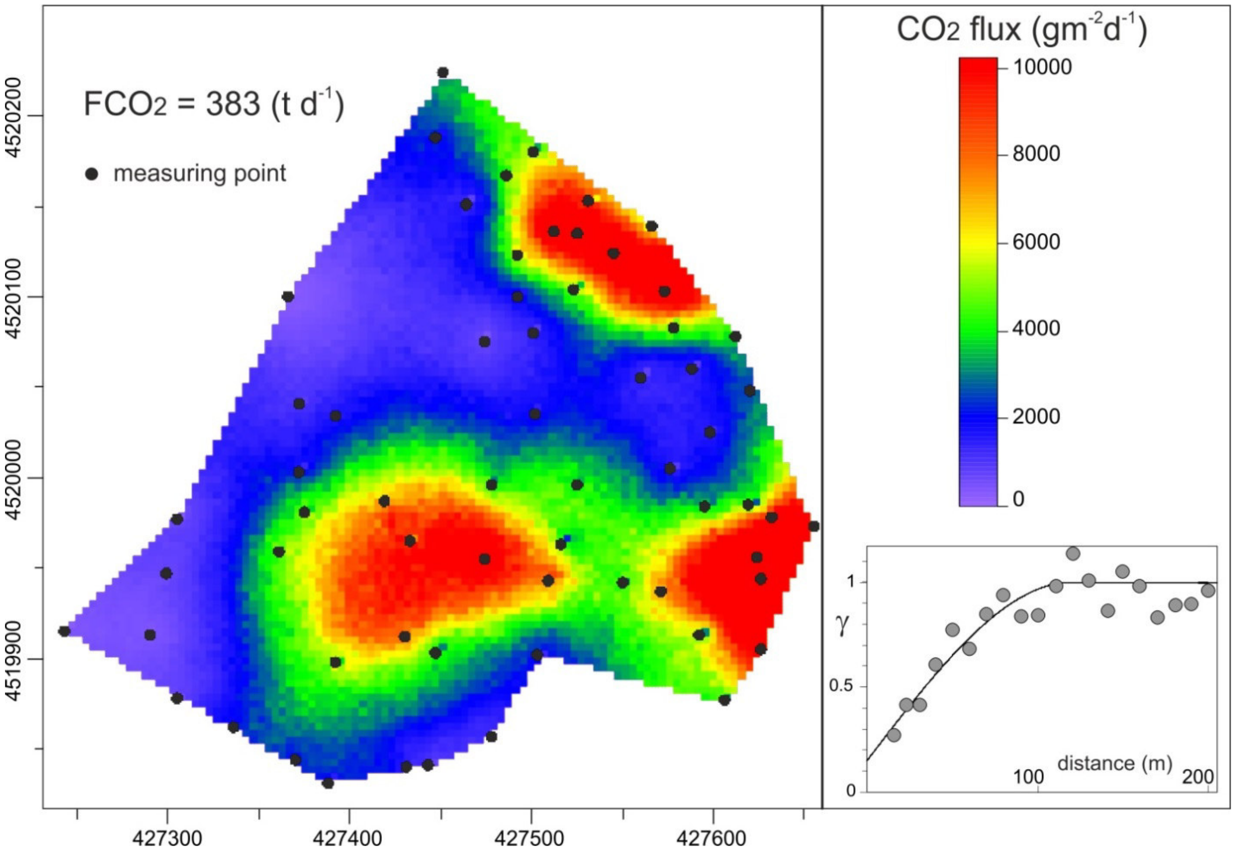


Fig. 9. Deep condensation rate and hydrothermal earthquakes occurrence. a) results of the steam mass balance involved in the degassing process (see the text); b) D*eep condensate* rate vs the monthly number of 'hydrothermal' earthquakes (grey histogram); c) normalized 'hydrothermal' earthquakes occurrence and normalized mean of deep condensate rate (six month values). See Fig. 7 for the definition of 'hydrothermal' earthquakes.

Supplementary Material



Supplementary Fig. S1. Map of the mean CO_2 flux of the target area. The map was produced by using the mean of the CO_2 fluxes measured in the 149 campaigns. In the figure is reported also the experimental variogram of the normal score of the CO_2 flux and the corresponding variogram model.

Supplementary Data File S1. Data sets: Bocca Nuova (BG) and Bocca Grande (BN) fumaroles composition; soil CO_2 flux measurements at 63 locations in the Solfatara target area; total CO_2 output target area (FCO2); Total CO_2 output form Solfatara DDS; CO_2 flux from Pisciarelli Vent; RSAM at CPIS station; Air CO_2 concentration at Pisciarelli; 2004-2020 earthquakes.